Supporting Information-

On the local charge inhomogeneity and lithium distribution in the superionic argyrodites Li_6PS_5X (X = Cl, Br, I)

Nicolò Minafra[a,b], Marvin A. Kraft[a,b], Tim Bernges[a,b], Cheng Li[c], Roman Schlem[a,b], Benjamin J. Morgan[d], Wolfgang G. Zeier*[a,b]

[a]*Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, D-35392 Giessen, Germany.*

[b]*Center for Materials Research (LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 16, D-35392 Giessen, Germany.*

[c]*Jülich Centre for Neutron Science (JCNS), Forschungszentrum Jülich GmbH, Outstation at SNS, 1 Bethel Valley Road, Oak Ridge, Tennessee 37831-6473, United States*

[d]*Department of Chemistry, University of Bath, Claverton Down BA2 7AY, United Kingdom*

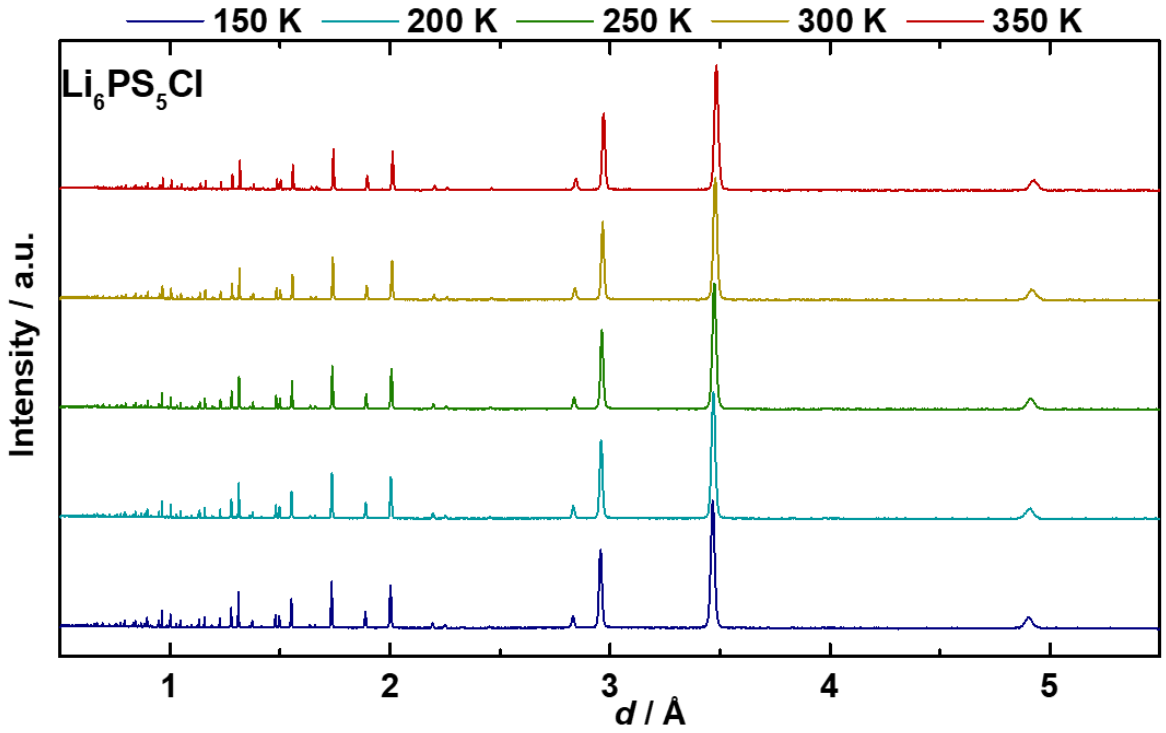

Figure S1: Neutron powder diffraction data of Li_6PS_5Cl measured at different temperatures. The refined structures are available in CIF format.

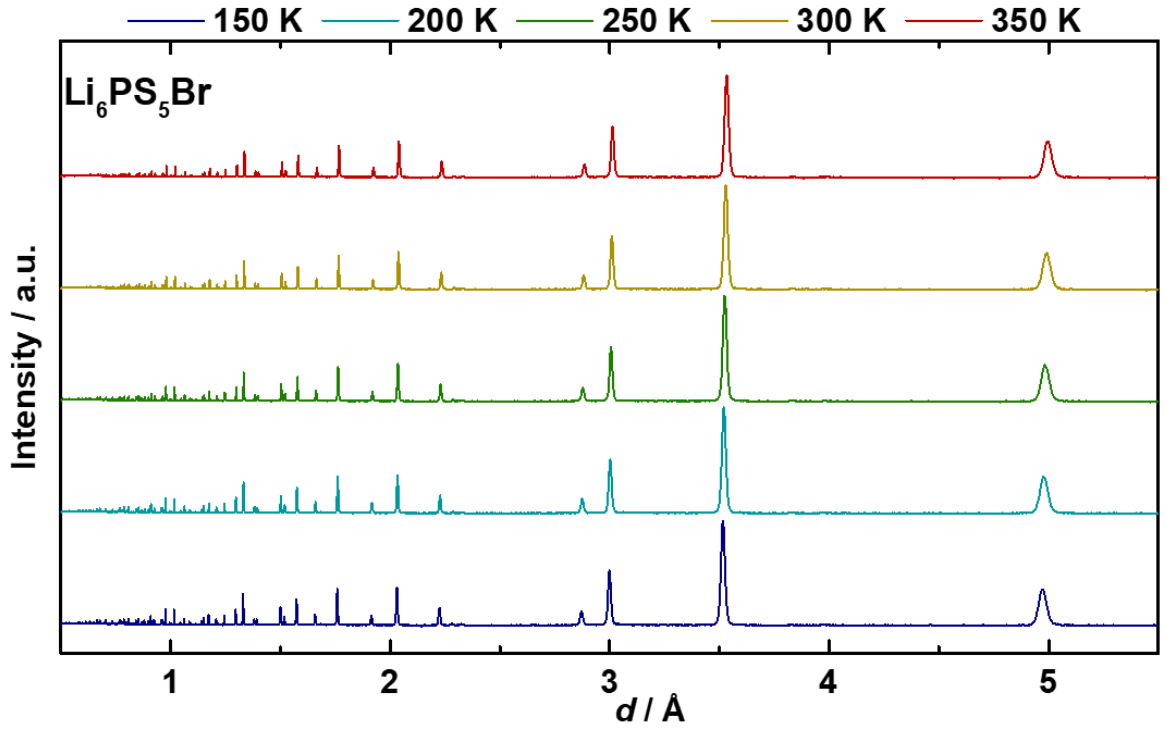

Figure S2: Neutron powder diffraction data of Li_6PS_5Br measured at different temperatures. The refined structures are available in CIF format.

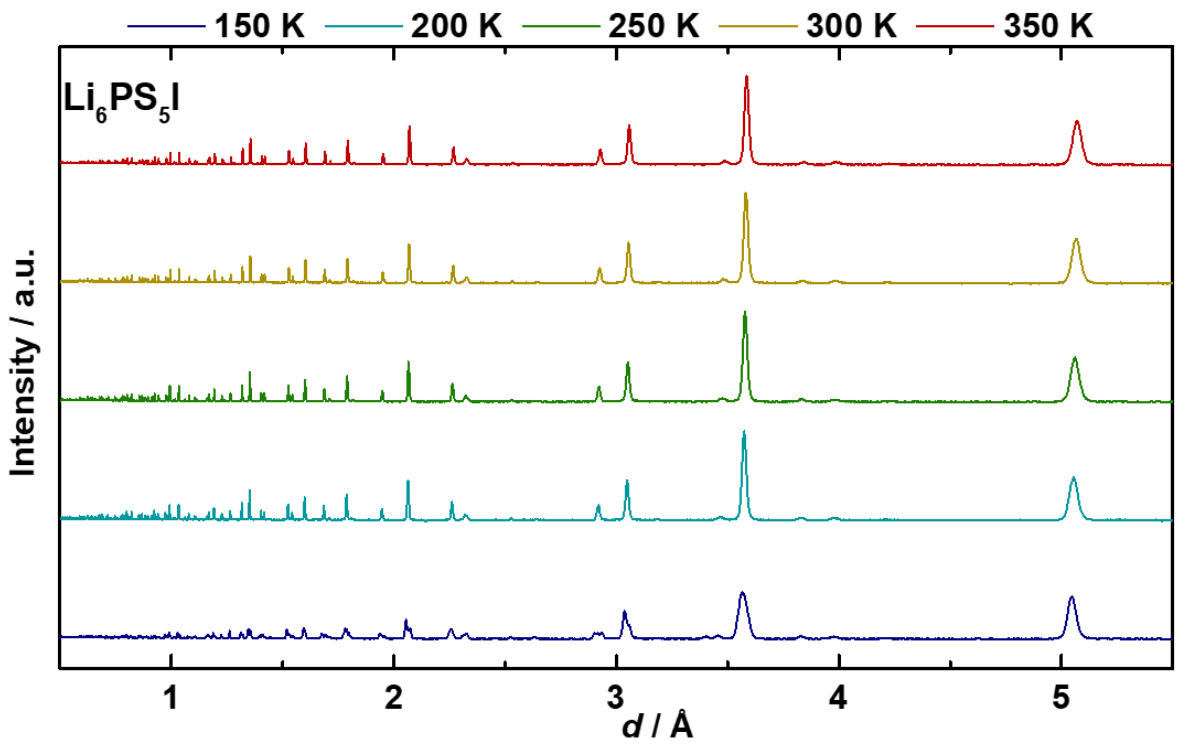

Figure S3: Neutron powder diffraction data of Li_6PS_5I measured at different temperatures. The refined structures are available in CIF format.

Table S1: Coordinates of all possible lithium sites in the Li_6PS_5X structure utilized as starting point for the refinements.

Position	Wyckoff Site	x/*a*	y/*b*	z/*c*
T1	16*e*	0.9	0.9	0.6
T2	48*h*	0.25	0.433	0.933
T3	4*c*	0.25	0.25	0.25
T4	16*e*	0.15	0.15	0.15
T5	48*h*	0.304	0.025	0.695
T5a	24*g*	0.25	0.009	0.75

Table S2: Constraints used to refine the Li_6PS_5Cl structure from powder ToF neutron diffraction data.

Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
LiT5	48*h*	*Pos1*	*Pos2*	1-*Pos1*	*Occ1*	*Var1*
LiT2	48*h*	*Pos3*	*Pos4*	0.5+*Pos4*	0.5-*Occ1*	*Var2*
Cl1	4*a*	0	0	0	*Occ2*	*Var3*
Cl2	4*d*	0.25	0.25	0.75	1-*Occ2*	*Var4*
P1	4*b*	0	0	0.5	1	*Var5*
S1	4*d*	0.25	0.25	0.75	*Occ2*	*Var4*
S2	16*e*	*Pos5*	-*Pos5*	0.5+*Pos5*	1	*Var6*
S3	4*a*	0	0	0	1-*Occ2*	*Var3*

Table S3: Constraints used to refine the Li_6PS_5Br structure from powder ToF neutron diffraction data.

Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
LiT5	48*h*	*Pos1*	*Pos2*	1-*Pos1*	*Occ1*	*Var1*
LiT2	48*h*	*Pos3*	*Pos4*	0.5+*Pos4*	*Occ2*	*Var2*
LiT5a	24*g*	0.25	*Pos5*	0.75	1-2·*Occ1*-2·*Occ2*	*Var3*
Br1	4*a*	0	0	0	*Occ3*	*Var4*
Br2	4*d*	0.25	0.25	0.75	1-*Occ3*	*Var5*
P1	4*b*	0	0	0.5	1	*Var6*
S1	4*d*	0.25	0.25	0.75	*Occ3*	*Var5*
S2	16*e*	*Pos6*	-*Pos6*	0.5+*Pos6*	1	*Var7*
S3	4*a*	0	0	0	1- *Occ3*	*Var4*

Table S4: Constraints used to refine the Li_6PS_5I structure from powder ToF neutron diffraction data.

Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
LiT5	48*h*	*Pos1*	*Pos2*	1-*Pos1*	*Occ1*	*Var1*
LiT5a	24*g*	0.25	*Pos3*	0.75	1-2·*Occ1*	*Var2*
I1	4*a*	0	0	0	1	*Var3*
P1	4*b*	0	0	0.5	1	*Var4*
S1	4*d*	0.25	0.25	0.75	1	*Var5*
S2	16*e*	*Pos4*	*-Pos4*	0.5+*Pos4*	1	*Var6*

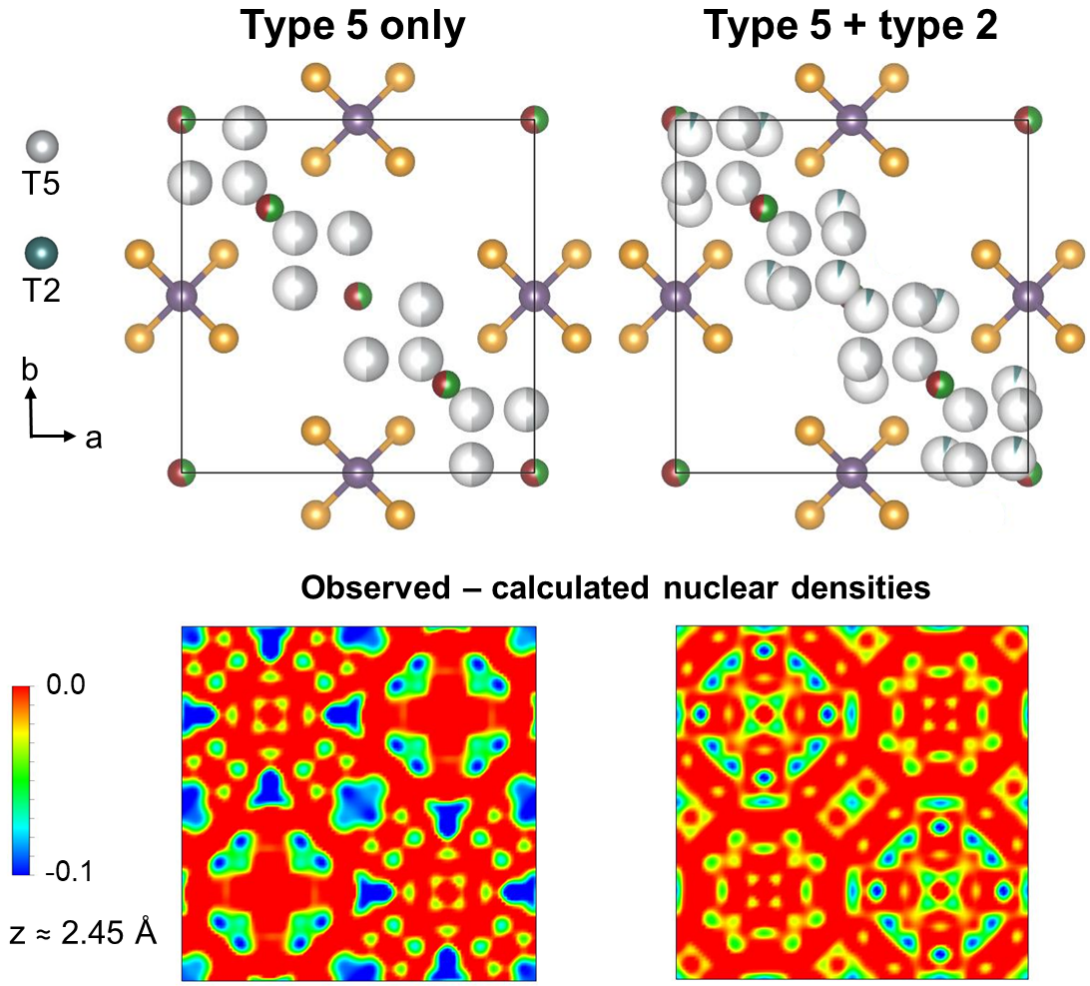

Figure S4: Exemplary difference Fourier maps for Li_6PS_5Cl, showing the need to include the type 2 lithium sites in the structural model.

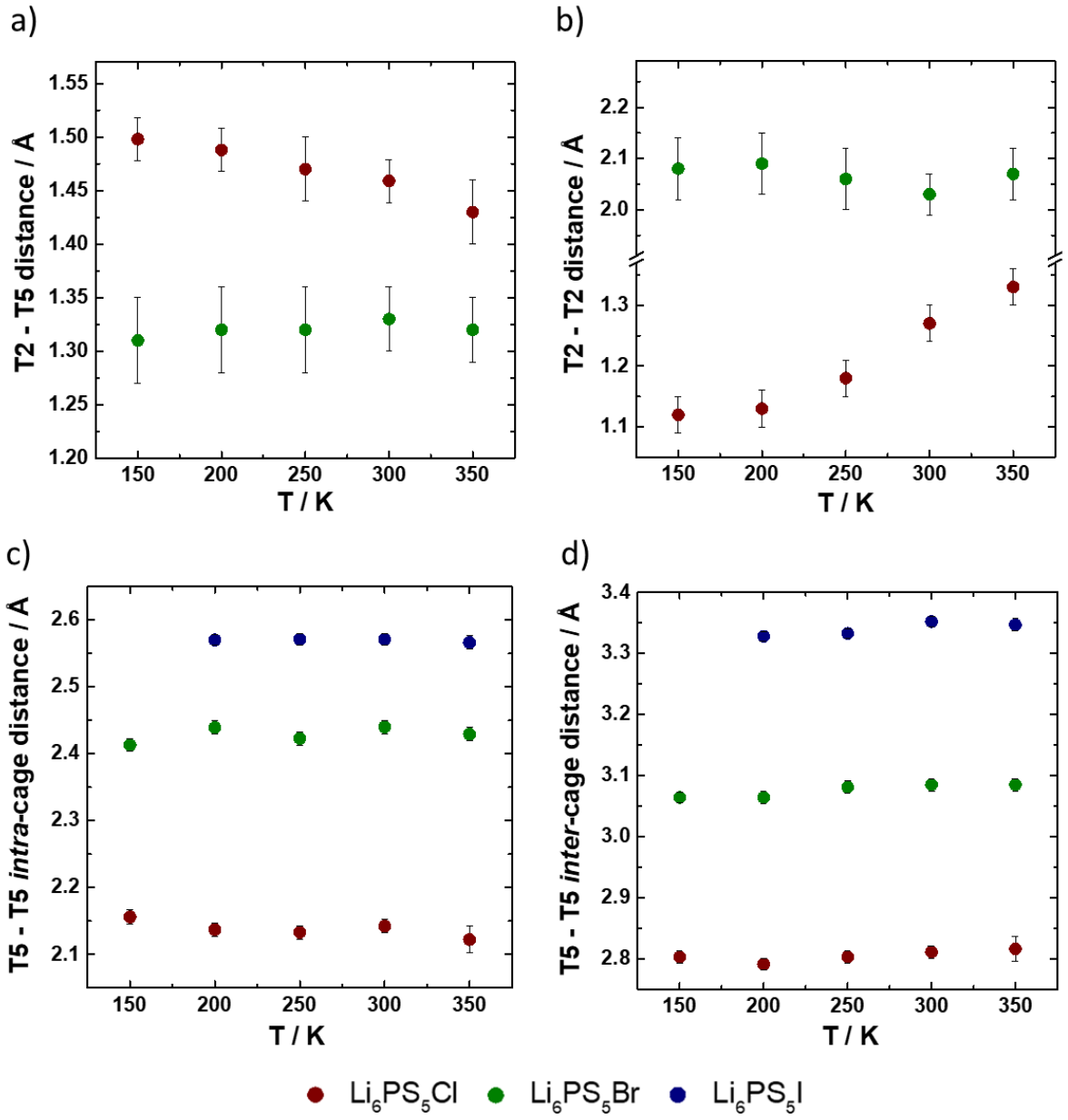

Figure S5: Li – Li distances relative to (a) T2 – T5 and (b) T2 – T2, in comparison to (c) T5 – T5 intra-cage and (d) T5 – T5 inter-cage at different temperatures for Li_6PS_5X.